DESCRIPTION

MANUFACTURING PROCESS FOR MEMBRANE-ELECTRODE ASSEMBLIES

5   **FIELD OF THE INVENTION**

The present invention relates to a manufacturing process for membrane-electrode assemblies (MEA), and more particularly to an MEA manufacturing process that can combine an electrolyte membrane and electrode substrates with good

10   adhesion to provide high joint reliability.

BACKGROUND OF THE INVENTION

MEA is an integral assembly generally consisting of an electrolyte membrane (proton conductive membrane) and

15   electrode substrates. Conventional production of MEA has been carried out by sandwiching an electrolyte membrane between two electrode substrates and hot pressing them to form an anode/electrolyte/cathode assembly.

Proton conductive membranes based on sulfonated

20   perfluorohydrocarbon, typically Nafion® membranes, are thermoplastic and can be thermocompression bonded with electrodes. On the other hand, electrolyte membranes of aromatic polymers such as sulfonated polyarylenes have heat resistance so that the thermocompression bonding often fails

to achieve sufficient bond strength unless carried out at high

temperatures that will cause deterioration of metallic

catalysts.

Film casting is a method to make electrolyte membranes

5   by flow casting a solution of a polymer in an organic solvent

on a substrate, followed by drying the formed coating. In the

film casting method, highly dipolar and aprotic organic

solvents are generally used to dissolve highly polar polymers

with ion-exchange groups, such as proton conductive polymers.

10   These dipolar solvents, due to their high boiling points, are

not completely removed upon drying and as a result remain in

the final electrolyte membranes. The electrolyte membranes

that contain such polar solvents in high concentrations cannot

be adequately thermocompression bonded with electrode

15 . substrates, causing poor interlaminar bond strength of MEA.

OBJECT OF THE INVENTION

In consideration of these prior art problems, the

invention has an object of providing a manufacturing process

20   for MEA that enables sufficient bond strength among an

electrolyte membrane and electrode substrates even when the

electrolyte membrane comprises a heat-resistant material such

as an aromatic polymer.

SUMMARY OF THE INVENTION

The invention achieves the above object by providing the following:

(1) A process of manufacturing membrane-electrode assemblies, said process comprising pressure bonding an electrolyte membrane with electrode substrates to form a membrane-electrode assembly, wherein a good solvent for the electrolyte membrane is applied to at least one of facing surfaces of the opposed electrode substrate and the electrolyte membrane prior to the pressure bonding.

(2) The process as described in (1), wherein a good solvent for the electrolyte membrane is applied to both of the facing surfaces of the opposed electrolyte membrane and the electrode substrate.

(3) The process as described in (1) or (2), wherein the electrolyte membrane is a film produced by a film casting method in which a solution of a proton conductive polymer in an organic solvent is flow cast on a substrate and wherein the electrolyte membrane contains the residual solvent in an amount of 5 parts by weight or less based on 100 parts by weight of the proton conductive polymer.

(4) The process as described in any one of (1) to (3), wherein the electrolyte membrane comprises a sulfonated aromatic polymer.

(5) The process as described in (4), wherein the good solvent for the electrolyte membrane is an aprotic dipolar solvent.

(6) The process as described in (4), wherein the

5 sulfonated aromatic polymer is a sulfonated polyarylene.

DETAILED DESCRIPTION OF THE INVENTION

Hereinbelow, the process for the production of MEA according to the invention will be described in detail.

10 The process comprises pressure bonding an electrolyte membrane with electrode substrates to form a membrane-electrode assembly. In the pressure bonding, a good solvent for the electrolyte membrane is applied to at least one of facing surfaces of the opposed electrolyte membrane and

15 electrode substrate and thereafter the electrolyte membrane and the electrode substrates are pressure bonded.

(Electrode substrates)

The electrode substrates for use in the invention each may be obtained by coating a gas diffusion electrode base with

20 a paste that contains fine particles of hydrogen reduction catalyst supported on conductive porous particles, and a proton conductive polymeric electrolyte component.

The conductive porous particles include those having bulky structures and large specific surface areas, such as

Ketjen black and acetylene black. Exemplary hydrogen

reduction catalysts include noble metals such as platinum,

palladium, ruthenium and rhodium; and alloys of these noble

metals with other metals such as chromium, molybdenum,

5   tungsten, titanium, zirconium and cobalt. The metallic

catalyst will be supported on the conductive porous particles

in amounts of 10 to 60 wt%.

A doctor blade or spraying may be employed for applying

the paste containing those fine catalyst particles and

10   polymeric electrolyte component on the porous gas diffusion

electrode base such as carbon paper or carbon cloth.

The electrode substrate will range in thickness from 5
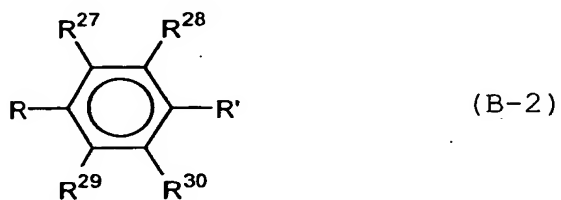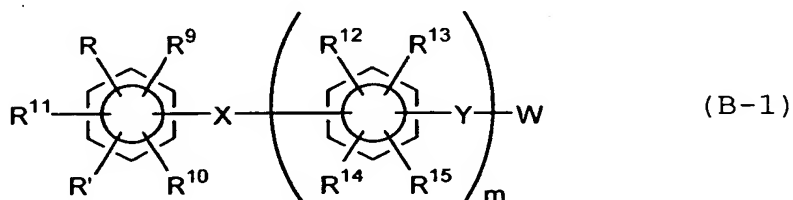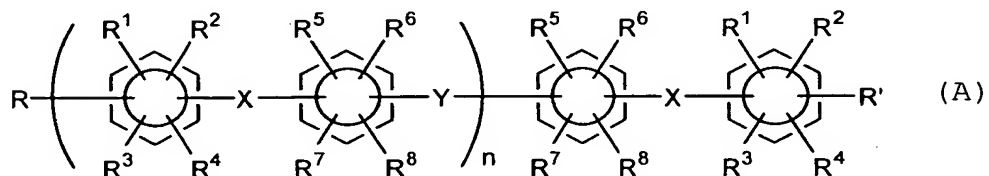
to 100μm, and preferably from 5 to 50μm.

(Electrolyte membrane)

15   The electrolyte membrane for use in the invention

comprises a proton conductive polymer. Exemplary proton

conductive polymers include sulfonated polyarylenes,

sulfonated polyarylene ethers, sulfonated polyarylene ketones,

sulfonated polyether ether ketones, sulfonated polyimides,

20   sulfonated polybenzimidazoles and sulfonated

tetrafluoroethylene copolymers. In order to obtain MAE with

good electrical properties, the sulfonated aromatic polymers,

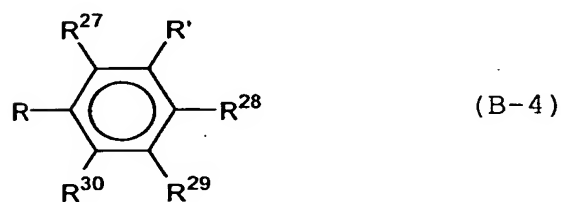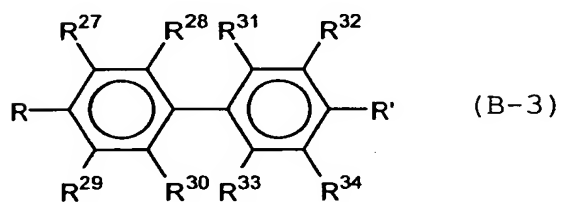particularly the sulfonated polyarylenes, are preferable.

The sulfonated polyarylene may be prepared by

sulfonating a polymer that results from the reaction of a
monomer (A) of the following formula (A) with at least one
monomer (B) having any of the following formulae (B-1) to (B-4).

$$R \left(\underset{\underset{R^3 \quad R^4}{}}{\overset{\overset{R^1 \quad R^2}{}}{\bigcirc}} - X - \underset{\underset{R^7 \quad R^8}{}}{\overset{\overset{R^5 \quad R^6}{}}{\bigcirc}} - Y \right)_n \underset{\underset{R^7 \quad R^8}{}}{\overset{\overset{R^5 \quad R^6}{}}{\bigcirc}} - X - \underset{\underset{R^3 \quad R^4}{}}{\overset{\overset{R^1 \quad R^2}{}}{\bigcirc}} - R' \qquad (A)$$

$$R^{11} \underset{\underset{R' \quad R^{10}}{}}{\overset{\overset{R \quad R^9}{}}{\bigcirc}} - X \left(\underset{\underset{R^{14} \quad R^{15}}{}}{\overset{\overset{R^{12} \quad R^{13}}{}}{\bigcirc}} - Y \right)_m W \qquad (B-1)$$

$$R - \underset{\underset{R^{29} \quad R^{30}}{}}{\overset{\overset{R^{27} \quad R^{28}}{}}{\bigcirc}} - R' \qquad (B-2)$$

$$R - \underset{\underset{R^{29} \quad R^{30}}{}}{\overset{\overset{R^{27} \quad R^{28}}{}}{\bigcirc}} \underset{\underset{R^{33} \quad R^{34}}{}}{\overset{\overset{R^{31} \quad R^{32}}{}}{\bigcirc}} - R' \qquad (B-3)$$

$$R - \underset{\underset{R^{30} \quad R^{29}}{}}{\overset{\overset{R^{27} \quad R'}{}}{\bigcirc}} - R^{28} \qquad (B-4)$$

In the formula (A), R and R', which may be the same or different, are each a halogen atom other than a fluorine atom or an $-OSO_2Z$ group (where Z is an alkyl group, a fluorine-substituted alkyl group or an aryl group).

5   Exemplary groups indicated by Z include:

alkyl groups such as methyl and ethyl groups;

fluorine-substituted alkyl groups such as a trifluoromethyl group; and

aryl groups such as phenyl and p-tolyl groups.

10   R^1 to R^8, which may be the same or different, are each at least one atom or group selected from the group consisting of a hydrogen atom, a fluorine atom, and alkyl, fluorine-substituted alkyl, allyl and aryl groups.

Examples of the alkyl groups include methyl, ethyl,
15 propyl, butyl, amyl and hexyl groups. Of these, methyl and ethyl groups are preferred.

Examples of the fluorine-substituted alkyl groups include trifluoromethyl, perfluoroethyl, perfluoropropyl, perfluorobutyl, perfluoropentyl and perfluorohexyl groups.
20 Of these, trifluoromethyl and pentafluoroethyl groups are preferred.

Examples of the allyl groups include a propenyl group.

Examples of the aryl groups include phenyl and pentafluorophenyl groups.

X is a divalent electron-withdrawing group. Examples thereof include -CO-, -CONH-, $-(CF_2)_p-$ (wherein p is an integer of 1 to 10), $-C(CF_3)_2-$, -COO-, -SO- and $-SO_2-$.

The electron-withdrawing group is defined as a group with a Hammett substituent constant of not less than 0.06 at the m-position of a phenyl group and not less than 0.01 at the p-position.

Y is a divalent electron-donating group. Examples thereof include -O-, -S-, -CH=CH-, $-C{\equiv}C-$ and groups represented by the following formulae:
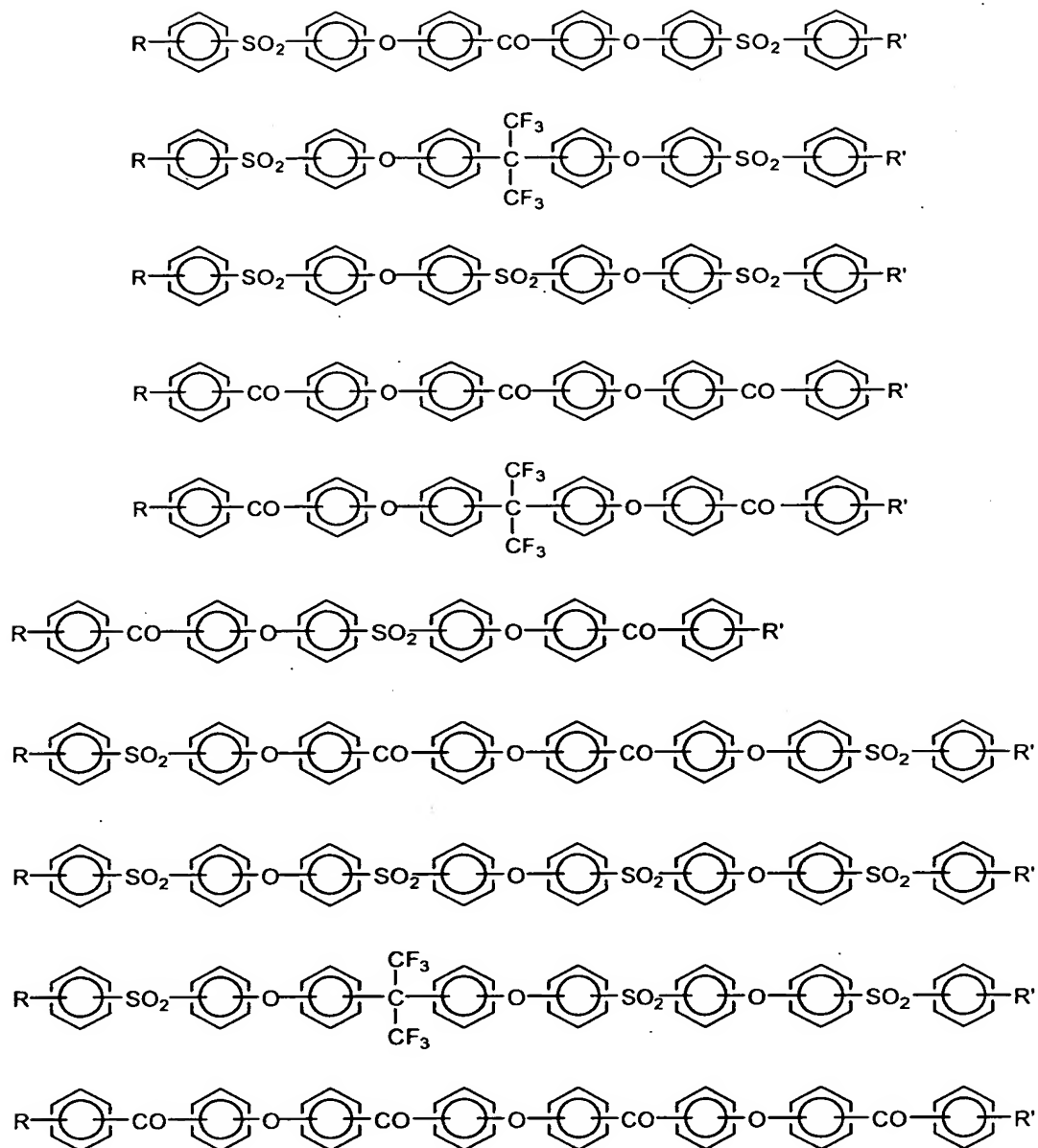
 and
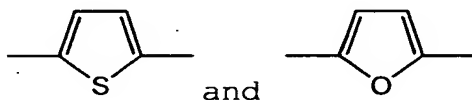
wherein n is 0 or a positive integer of up to 100, and preferably up to 80.

Exemplary monomers of the formula (A) in which n is 0 include 4,4'-dichlorobenzophenone, 4,4'-dichlorobenzanilide, bis(chlorophenyl)difluoromethane, 2,2-bis(4-chlorophenyl)hexafluoropropane, 4-chlorobenzoic acid-4-chlorophenyl, bis(4-chlorophenyl)sulfoxide, bis(4-chlorophenyl)sulfone, corresponding compounds to these compounds except that the chlorine atom is replaced with a bromine or an iodine atom, and corresponding compounds to the above compounds except that at least one of the halogen atoms

substituted at the 4-position is altered to a substituent at

the 3-position.

Exemplary monomers of the formula (A) in which n is 1

include 4,4'-bis(4-chlorobenzoyl)diphenyl ether,

5   4,4'-bis(4-chlorobenzoylamino)diphenyl ether,

4,4'-bis(4-chlorophenylsulfonyl)diphenyl ether,

4,4'-bis(4-chlorophenyl)diphenyl ether dicarboxylate,

4,4'-bis((4-chlorophenyl)-1,1,1,3,3,3-hexafluoropropyl)

diphenyl ether,

10   4,4'-bis((4-chlorophenyl)tetrafluoroethyl)diphenyl ether,

corresponding compounds to these compounds except that the

chlorine atom is replaced with a bromine or an iodine atom,

corresponding compounds to the above compounds except that the

halogen substitution occurs at the 3-position in place of the

15   4-position, and corresponding compounds to the above compounds

except that at least one of the substituent groups at the

4-position in the diphenyl ether is altered to a substituent

at the 3-position.

Also available as the monomer (A) are

20   2,2-bis(4-(4-(4-chlorobenzoyl)phenoxy)phenyl)-1,1,1,3,3,3-

hexafluoropropane, bis(4-(4-(4-chlorobenzoyl)

phenoxy)phenyl)sulfone, and compounds represented by the

following formulae:

$$R-\bigcirc-SO_2-\bigcirc-O-\bigcirc-CO-\bigcirc-O-\bigcirc-SO_2-\bigcirc-R'$$

$$R-\bigcirc-SO_2-\bigcirc-O-\bigcirc-\overset{\overset{CF_3}{|}}{\underset{\underset{CF_3}{|}}{C}}-\bigcirc-O-\bigcirc-SO_2-\bigcirc-R'$$

$$R-\bigcirc-SO_2-\bigcirc-O-\bigcirc-SO_2-\bigcirc-O-\bigcirc-SO_2-\bigcirc-R'$$

$$R-\bigcirc-CO-\bigcirc-O-\bigcirc-CO-\bigcirc-O-\bigcirc-CO-\bigcirc-R'$$

$$R-\bigcirc-CO-\bigcirc-O-\bigcirc-\overset{\overset{CF_3}{|}}{\underset{\underset{CF_3}{|}}{C}}-\bigcirc-O-\bigcirc-CO-\bigcirc-R'$$

$$R-\bigcirc-CO-\bigcirc-O-\bigcirc-SO_2-\bigcirc-O-\bigcirc-CO-\bigcirc-R'$$

$$R-\bigcirc-SO_2-\bigcirc-O-\bigcirc-CO-\bigcirc-O-\bigcirc-CO-\bigcirc-O-\bigcirc-SO_2-\bigcirc-R'$$

$$R-\bigcirc-SO_2-\bigcirc-O-\bigcirc-SO_2-\bigcirc-O-\bigcirc-SO_2-\bigcirc-O-\bigcirc-SO_2-\bigcirc-R'$$

$$R-\bigcirc-SO_2-\bigcirc-O-\bigcirc-\overset{\overset{CF_3}{|}}{\underset{\underset{CF_3}{|}}{C}}-\bigcirc-O-\bigcirc-SO_2-\bigcirc-O-\bigcirc-SO_2-\bigcirc-R'$$

$$R-\bigcirc-CO-\bigcirc-O-\bigcirc-CO-\bigcirc-O-\bigcirc-CO-\bigcirc-O-\bigcirc-CO-\bigcirc-R'$$

For example, the monomer (A) may be synthesized by the

5   process given below.

First, an alkali metal such as lithium, sodium or

potassium, or an alkali metal compound such as alkali metal

hydride, alkali metal hydroxide or alkali metal carbonate, is

added to bisphenols combined together by the

electron-withdrawing group for the purpose of converting them

into a corresponding alkali metal salt of bisphenol. This

addition is made in a polar solvent of high dielectric constant,

5   such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide,

sulfolane, diphenyl sulfone or dimethyl sulfoxide.

The alkali metal or alkali metal compound will be

generally used in slight excess relative to the hydroxyl groups

of the bisphenol, for example in an equivalent amount 1.1 to

10   2 times, and preferably 1.2 to 1.5 times with respect to the

amount of hydroxyl groups.

Thereafter, the alkali metal salt of bisphenol is reacted

with a halogen-substituted, e.g. fluorine- or

chlorine-substituted, aromatic dihalide compound which has

15   been activated by the electron-withdrawing groups, in the

presence of a solvent that can form an azeotropic mixture with

water, such as benzene, toluene, xylene, hexane, cyclohexane,

octane, chlorobenzene, dioxane, tetrahydrofuran, anisole or

phenetole. Examples of the above aromatic dihalide compound

20   include 4,4'-difluorobenzophenone,

4,4'-dichlorobenzophenone, 4,4'-chlorofluorobenzophenone,

bis(4-chlorophenyl)sulfone, bis(4-fluorophenyl)sulfone,

4-fluorophenyl-4'-chlorophenylsulfone,

bis(3-nitro-4-chlorophenyl)sulfone,

2,6-dichlorobenzonitrile, 2,6-difluorobenzonitrile,

hexafluorobenzene, decafluorobiphenyl,

2,5-difluorobenzophenone and

1,3-bis(4-chlorobenzoyl)benzene.

5   From the viewpoint of reactivity, the aromatic dihalide

compound is desirably a fluorine compound. But taking the

subsequent aromatic coupling reaction into account, the

aromatic nucleophilic substitution reaction should be

designed to take place so as to yield a molecule having a

10   chlorine atom at its end(s). The active aromatic dihalide

compound may be used in an amount 2 to 4 molar times, and

preferably 2.2 to 2.8 molar times the amount of the bisphenol.

The reaction temperature is in the range of 60 to 300°C, and

preferably 80 to 250°C. The reaction time ranges from 15

15   minutes to 100 hours, and preferably from 1 to 24 hours.

        Optimally, the active aromatic dihalide compound is a

chlorofluoro compound as shown in the formula hereinbelow that

has two halogen atoms different in reactivity from each other.

The use of this compound is advantageous in that the fluorine

20   atom will preferentially undergo the nucleophilic

substitution reaction with phenoxide so that the objective

chlorine-terminated active compound may be obtained.
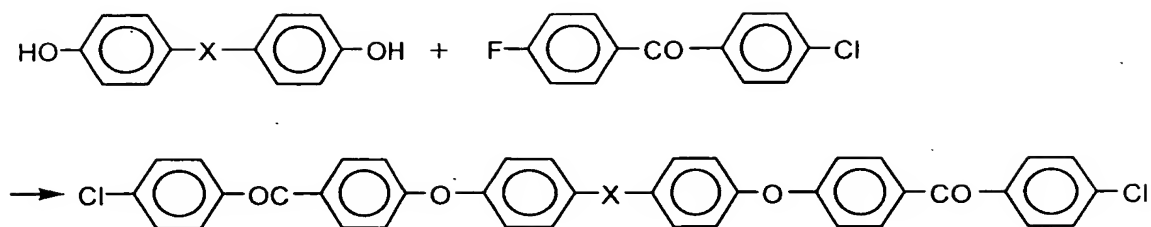
wherein X is as defined in the formula (A).

Other exemplary methods for the synthesis of the monomer

5   (A) include JP-A-2(1990)-159, in which the nucleophilic

substitution reaction is carried out combined with an

electrophilic substitution reaction to synthesize an

objective flexible compound comprising the

electron-withdrawing and electron-donating groups.

10   Specifically, the aromatic dihalide compound activated

by the electron-withdrawing group, such as

bis(4-chlorophenyl)sulfone, is subjected to the nucleophilic

substitution reaction with a phenol compound; thereafter the

resultant bis-phenoxy compound is subjected to Friedel-Crafts

15   reaction with, for example, 4-chlorobenzoyl chloride to obtain

an objective compound.

In the synthesis, any of the above-exemplified aromatic

dihalide compounds can be used as the aromatic dihalide

compound activated by the electron-withdrawing group. The

20   phenol compound may be substituted, but is preferably

unsubstituted from the viewpoints of heat resistance and

flexibility. When substituted, the substituted phenol

compound is preferably an alkali metal salt. Any of the alkali

metal compounds listed above can be used in the substitution

reaction for the phenol compound. The alkali metal compound

5   is used in an amount 1.2 to 2 molar times the amount of the

phenol. In the reaction, the aforesaid polar solvent or the

azeotropic solvent with water may be employed.

To obtain the objective compound, the bis-phenoxy

compound is reacted with chlorobenzoyl chloride as an

10   acylating agent, in the presence of an activator for the

Friedel-Crafts reaction, e.g., Lewis acid such as aluminum

chloride, boron trifluoride or zinc chloride. The

chlorobenzoyl chloride is used in an amount 2 to 4 molar times,

and preferably 2.2 to 3 molar times the amount of the

15   bis-phenoxy compound. The Friedel-Crafts reaction activator

is used in an equivalent amount 1.1 to 2 times relative to 1

mole of the active halide compound such as an acylating agent

chlorobenzoic acid. The reaction time is in the range of 15

minutes to 10 hours, and the reaction temperature is in the

20   range of -20 to 80°C. As a solvent, chlorobenzene,

nitrobenzene or the like that is inactive in the Friedel-crafts

reaction may be used.

The monomer (A) in which n is 2 or more may be synthesized

through polymerization in accordance with the above-mentioned

procedure. In this case, a bisphenol, which can supply ether

oxygen as the electron donating group Y in the monomer (A),

is combined with the electron-withdrawing group X of $>C=O$,

$-SO_2-$ and/or $>C(CF_3)_2$ (i.e., 2,2-bis(4-hydroxyphenyl)-

5   1,1,1,3,3,3-hexafluoropropane,

2,2-bis(4-hydroxyphenyl)ketone or 2,2-bis(4-hydroxyphenyl)

sulfone) and is reacted with an alkali metal compound; the

resultant alkali metal salt of bisphenol is then subjected to

a substitution reaction with an excess of the activated

10   aromatic halogen compound such as 4,4-dichlorobenzophenone or

bis(4-chlorophenyl)sulfone, in the presence of a polar solvent

such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide or

sulfolane.

        Examples of such monomers (A) include compounds

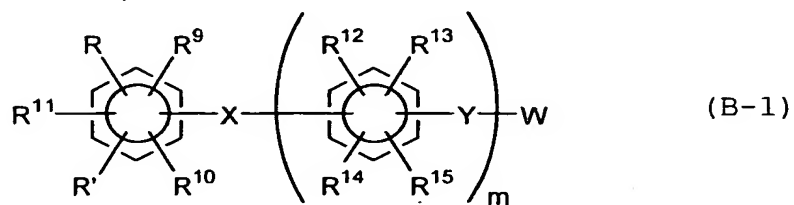15   represented by the following formulae:
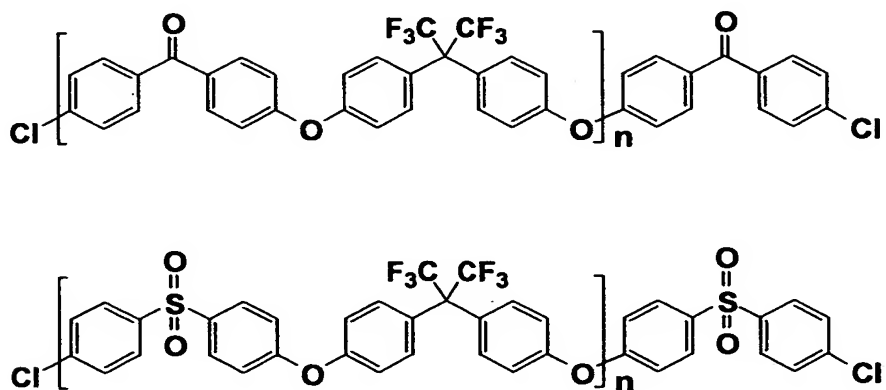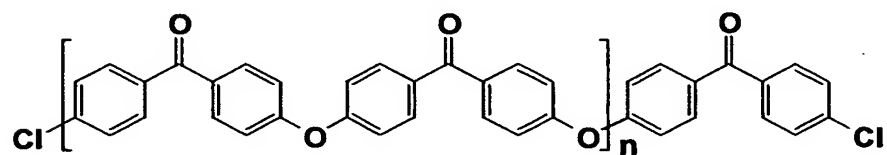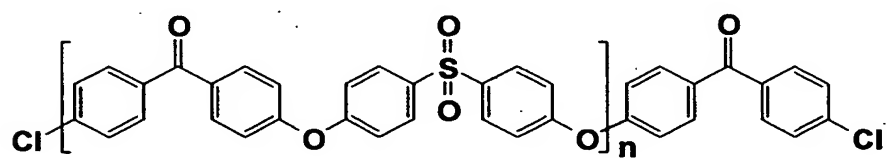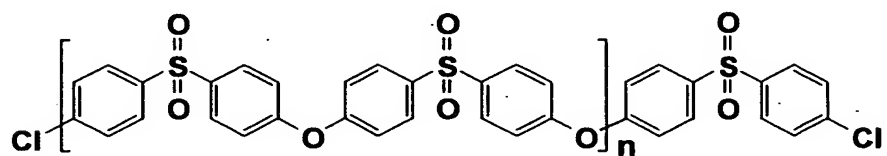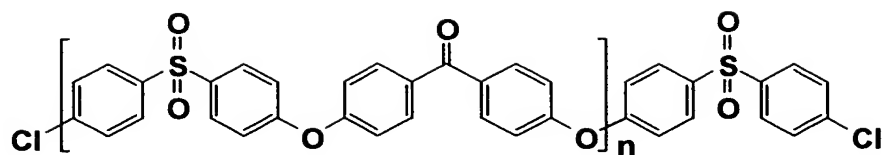
5   In the above formulae, n is 2 or greater, and preferably

from 2 to 100.

        Next, the monomers represented by the formulae (B-1) to

(B-4) will be described.

10   (B-1)

In the above formula, R and R' may be the same or different

and denote the same groups as defined in the formula (A).

R^9 to R^{15}, which may be the same or different, are each

at least one atom or group selected from a hydrogen atom, a
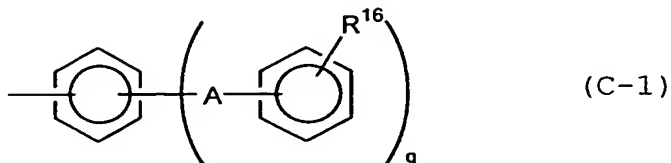
5   fluorine atom and an alkyl group.

The alkyl groups indicated by R^9 to R^{15} include the same

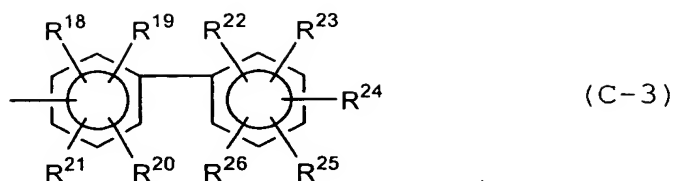alkyl groups as indicated by R^1 to R^8 in the formula (A)..

m is 0, 1 or 2.

X is a divalent electron-withdrawing group selected from

10   the same groups as defined with respect to X in the formula

(A).

Y is a divalent electron-donating group selected from

the same groups as defined with respect to Y in the formula

(A).

15   W denotes at least one group selected from the group

consisting of a phenyl group, a naphthyl group and groups

represented by the following formulae (C-1) to (C-3):

(C-1)

20

(C-2)

$$R^{18} \quad R^{19} \quad R^{22} \quad R^{23}$$

$$R^{21} \quad R^{20} \quad R^{26} \quad R^{25}$$

(C-3)
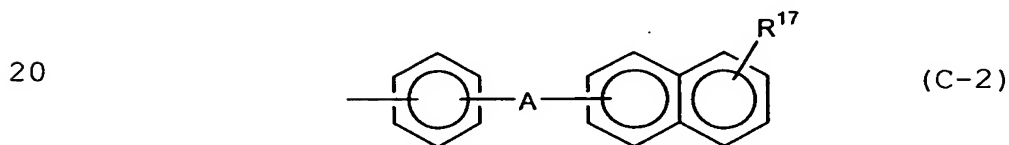
In the above formulae, A denotes an electron-donating group or a single bond. The electron-donating group may be

5   a divalent electron-donating group selected from the same groups as defined with respect to Y in the formula (A).

R^{16} and R^{17} are each a hydrogen atom, an alkyl group or an aryl group. Examples of the alkyl and aryl groups designated by R^{16} and R^{17} include the same alkyl and aryl groups

10   as indicated by R^1 to R^8 in the formula (A).

R^{18} to R^{26}, which may be the same or different, are each at least one atom or group selected from a hydrogen atom, a fluorine atom and an alkyl group. Examples of the alkyl groups designated by R^{18} to R^{26} include the same alkyl groups as
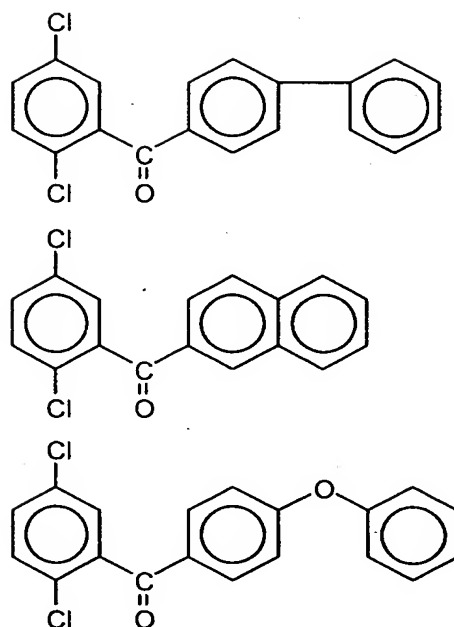
15   indicated by R^1 to R^8 in the formula (A).

q is 0 or 1.

Exemplary monomers represented by the formula (B-1) include compounds with the following formulae:
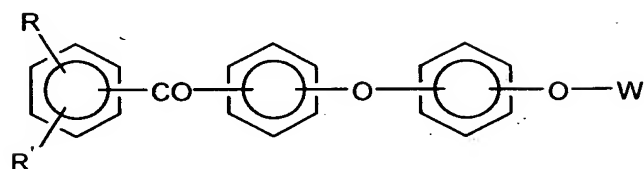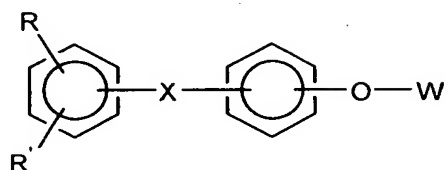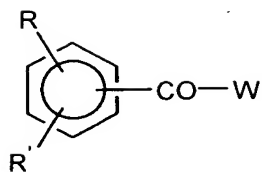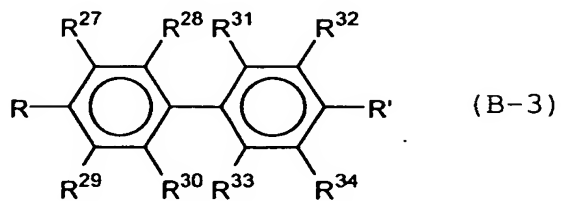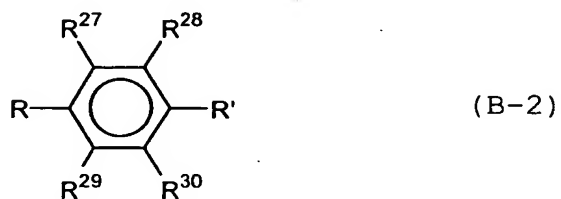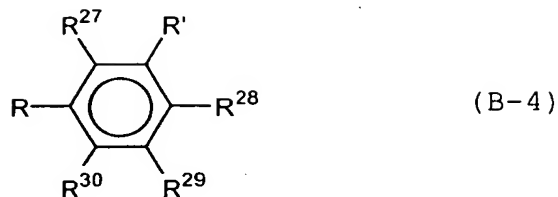
More specifically, the monomers of the formula (B-1) may be represented as follows:

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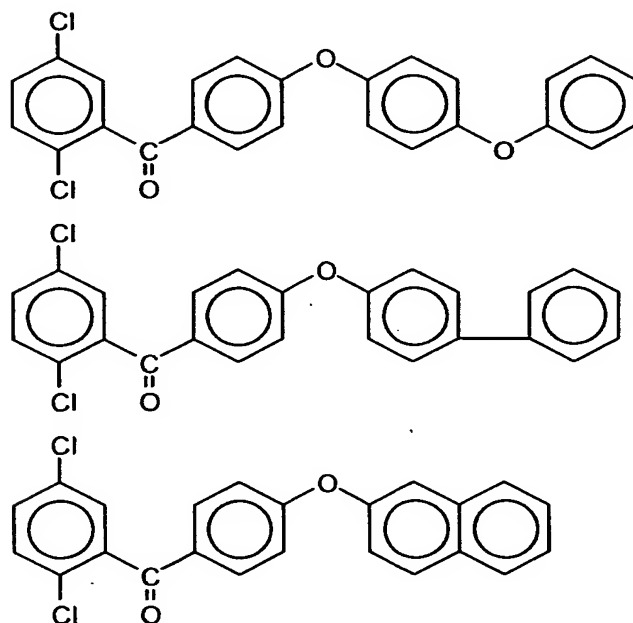
Further, corresponding compounds to the above compounds except that the chlorine atom is replaced with a bromine or

5   an iodine atom are also available.

(B-2)

(B-3)

10

$$\text{(B-4)}$$

In the formulae (B-2) to (B-4), R and R' may be the same

or different and denote the same groups as defined in the

5 formula (A).

R^{27} to R^{34}, which may be the same or different, are each

a hydrogen atom, a fluorine atom, an alkyl group, a

fluorine-substituted alkyl group, an aryl group or a group

represented by the following formula (D):

10

$$\text{(D)}$$
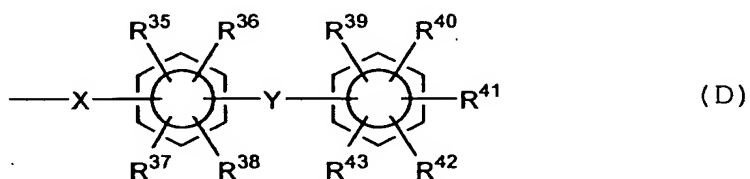
wherein R^{35} to R^{43}, which may be the same or different, are each

a hydrogen atom, a halogen atom, an alkyl group or a

15 fluorine-substituted alkyl group.

R^{27} to R^{34} and R^{35} to R^{43} may represent the same alkyl and

fluorine-substituted alkyl groups as indicated by R^1 to R^8.

R^{27} to R^{34} may represent the same aryl groups as indicated by

R^1 to R^8.

X denotes a divalent electron-withdrawing group selected from the same groups as defined with respect to X in the formula (A).

Y denotes a divalent electron-donating group selected from the same groups as defined with respect to Y in the formula (A).

Examples of the monomers having the formula (B-2) include p-dichlorobenzene, p-dimethylsulfonyloxybenzene, 2,5-dichlorotoluene, 2,5-dimethylsulfonyloxybenzene, 2,5-dichloro-p-xylene, 2,5-dichlorobenzotrifluoride, 1,4-dichloro-2,3,5,6-tetrafluorobenzene, and corresponding compounds to these compounds except that the chlorine atom is replaced with a bromine or an iodine atom.

Examples of the monomers having the formula (B-3) include 4,4'-dimethylsulfonyloxybiphenyl, 4,4'-dimethylsulfonyloxy-3,3'-dipropenylbiphenyl, 4,4'-dibromobiphenyl, 4,4'-diiodobiphenyl, 4,4'-dimethylsulfonyloxy-3,3'-dimethylbiphenyl, 4,4'-dimethylsulfonyloxy-3,3'-difluorobiphenyl, 4,4'-dimethylsulfonyloxy-3,3',5,5'-tetrafluorobiphenyl, 4,4'-dibromooctafluorobiphenyl and 4,4'-dimethylsulfonyloxyoctafluorobiphenyl.

Examples of the monomers having the formula (B-4) include m-dichlorobenzene, m-dimethylsulfonyloxybenzene,

2,4-dichlorotoluene, 3,5-dichlorotoluene,

2,6-dichlorotoluene, 3,5-dimethylsulfonyloxytoluene,

2,6-dimethylsulfonyloxytoluene,

2,4-dichlorobenzotrifluoride, 3,5-dichlorobenzotrifluoride,

5   1,3-dibromo-2,4,5,6-tetrafluorobenzene, and corresponding

compounds to these compounds except that the chlorine atom is

replaced with a bromine or an iodine atom.

To synthesize the polyarylene, the monomers mentioned

above are reacted in the presence of a catalyst. The catalyst

10   used herein is a catalyst system containing a transition metal

compound. This catalyst system essentially contains (1) a

transition metal salt and a compound which functions as a ligand

(referred to as the "ligand component" hereinafter), or a

transition metal complex (including a copper salt) to which

15   a ligand(s) has been coordinated, and (2) a reducing agent.

A "salt" may be added to increase the polymerization rate.

Examples of the transition metal salt include nickel

compounds such as nickel chloride, nickel bromide, nickel

iodide and nickel acetylacetonate; palladium compounds such

20   as palladium chloride, palladium bromide and palladium iodide;

iron compounds such as iron chloride, iron bromide and iron

iodide; and cobalt compounds such as cobalt chloride, cobalt

bromide and cobalt iodide. Of these, nickel chloride and

nickel bromide are particularly preferred.

Examples of the ligand component include triphenylphosphine, 2,2'-bipyridine, 1,5-cyclooctadiene and 1,3-bis(diphenylphosphino)propane. Of these, triphenylphosphine and 2,2'-bipyridine are preferred. The ligand components may be used singly or in combination of two or more kinds.

Examples of the transition metal complex with coordinated ligands include

nickel chloride-bis(triphenylphosphine),

nickel bromide-bis(triphenylphosphine),

nickel iodide-bis(triphenylphosphine),

nickel nitrate-bis(triphenylphosphine),

nickel chloride(2,2'-bipyridine),

nickel bromide(2,2'-bipyridine),

nickel iodide(2,2'-bipyridine),

nickel nitrate(2,2'-bipyridine),

bis(1,5-cyclooctadiene)nickel,

tetrakis(triphenylphosphine)nickel,

tetrakis(triphenylphosphite)nickel and

tetrakis(triphenylphosphine)palladium. Of these, nickel chloride-bis(triphenylphosphine) and nickel chloride(2,2'-bipyridine) are preferred.

Examples of the reducing agent employable in the aforesaid catalyst system include iron, zinc, manganese,

aluminum, magnesium, sodium and calcium. Of these, zinc,

magnesium and manganese are preferable. These reducing agents

may be used in a more activated form brought about by contact

with an acid such as an organic acid.

5   Examples of the "salt" employable in the catalyst system

include sodium compounds such as sodium fluoride, sodium

chloride, sodium bromide, sodium iodide and sodium sulfate;

potassium compounds such as potassium fluoride, potassium

chloride, potassium bromide, potassium iodide and potassium

10   sulfate; and ammonium compounds such as tetraethylammonium

fluoride, tetraethylammonium chloride, tetraethylammonium

bromide, tetraethylammonium iodide and tetraethylammonium

sulfate. Of these, sodium bromide, sodium iodide, potassium

bromide, tetraethylammonium bromide and tetraethylammonium

15   iodide are preferred.

In respect of the proportion of the above components,

the transition metal salt or the transition metal complex is

usually used in an amount of 0.0001 to 10 mol, and preferably

0.01 to 0.5 mol based on 1 mol of the total monomers. If the

20   amount is less than 0.0001 mol, the polymerization may not

proceed sufficiently. Contrary, the amount exceeding 10 mol

may result in a lowered molecular weight of the polyarylene.

When the catalyst system contains the transition metal

salt and the ligand component, the ligand component usually

has an amount of 0.1 to 100 mol, and preferably 1 to 10 mol

based on 1 mol of the transition metal salt. If the amount

is less than 0.1 mol, the catalytic activity may become

insufficient. Contrary, the amount exceeding 100 mol may

5   result in a lowered molecular weight of the polyarylene.

The amount of the reducing agent is usually in the range

of 0.1 to 100 mol, and preferably 1 to 10 mol based on 1 mol

of the total monomers. If the reducing agent is used in an

amount of less than 0.1 mol, the polymerization may not proceed

10   sufficiently. Contrary, the amount thereof exceeding 100 mol

may make the purification of the resulting polymer more

difficult.

When the "salt" is used, the amount thereof is usually

0.001 to 100 mol, and preferably 0.01 to 1 mol based on 1 mol

15   of the total monomers. If the salt is used in an amount of

less than 0.001 mol, sufficient effect of increasing the

polymerization rate often cannot be obtained. Contrary, the

amount thereof exceeding 100 mol may result in difficult

purification of the resulting polymer.

20   Suitable solvents for the above polymerization include

tetrahydrofuran, cyclohexanone, dimethyl sulfoxide,

N,N-dimethylformamide, N,N-dimethylacetamide,

N-methyl-2-pyrrolidone, γ-butyrolactone and γ-butyrolactam.

Of these, tetrahydrofuran, N,N-dimethylformamide,

N,N-dimethylacetamide and N-methyl-2-pyrrolidone are

preferred. These polymerization solvents are desirably used

after dried sufficiently.

The concentration of the total monomers in the

5   polymerization solvent is usually in the range of 1 to 90 wt%,

and preferably 5 to 40 wt%.

The polymerization will be usually carried out at 0 to

200°C, and preferably 50 to 120°C, and over a period of 0.5

to 100 hours, and preferably 1 to 40 hours.

10   The polymerization of the monomer (A) having the formula

(A) with at least one monomer (B) represented by any of the

formulae (B-1) to (B-4) as described above yields a

polymerization solution containing the polyarylene.

The thus-obtained polyarylene, which has no sulfonic

15   acid groups, is then treated with a sulfonating agent by the

conventional technique, introducing thereinto sulfonic acid

groups. The polyarylene having sulfonic acid groups may be

thus obtained.

For introduction of sulfonic acid groups, the

20   polyarylene having no sulfonic acid groups may be treated with

a conventional sulfonating agent, such as sulfuric anhydride,

fuming sulfuric acid, chlorosulfonic acid, sulfuric acid or

sodium bisulfite, under known conditions (see Polymer

Preprints, Japan, vol. 42, No. 3, p. 730 (1993), Polymer

Preprints, Japan, vol. 42, No. 3, p. 736 (1994), Polymer

Preprints, Japan, vol. 42, No. 7, pp. 2490-2492 (1993)).

Specifically, the polyarylene having no sulfonic acid

groups is reacted with the sulfonating agent in the presence

5   or absence of a solvent. Examples of the solvent include

hydrocarbon solvents such as n-hexane; ether-based solvents

such as tetrahydrofuran and dioxane; aprotic polar solvents

such as dimethylacetamide, dimethylformamide and dimethyl

sulfoxide; and halogenated hydrocarbons such as

10   tetrachloroethane, dichloroethane, chloroform and methylene

chloride. Although the temperature in the sulfonation is not

specifically limited, it is usually in the range of -50 to 200°C,

and preferably -10 to 100°C. The reaction time is usually 0.5

to 1,000 hours, and preferably 1 to 200 hours.

15   In the invention, the sulfonated polyarylene will

contain sulfonic acid groups in an amount of 0.5 to 3 meq/g,

and preferably 0.8 to 2.8 meq/g. If the sulfonic acid group

content is less than 0.5 meq/g, the proton conductivity may

be insufficient. Contrary, when it exceeds 3 meq/g,

20   hydrophilicity is so increased that the resulting polymer

becomes water soluble or, if not water soluble, less durable.

The precursor polymer of the sulfonated polyarylene

(i.e., polyarylene prior to the sulfonation) has a

weight-average molecular weight of 10,000 to 1,000,000, and

preferably 20,000 to 800,000, in terms of polystyrene. When

the weight-average molecular weight is less than 10,000,

coating properties become so poor that cracks may form in the

resultant film, and also mechanical strength may be

5   insufficient. On the other hand, the weight-average molecular

weight exceeding 1,000,000 leads to bad solubility and high

solution viscosity, causing bad processability.

Meanwhile, the sulfonated polyarylene may be also

produced by hydrolysis of a polyarylene resulting from

10   homopolymerization of an aromatic sulfonate derivative

represented by the formula (E):

(E)
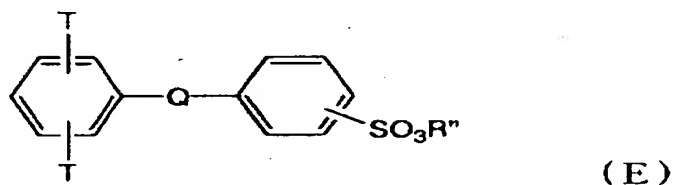
wherein T is a halogen atom other than a fluorine atom, an

$-OSO_3CH_3$ group or an $-OSO_3CF_3$ group; Q is a divalent organic

15   group; and R'' is a hydrocarbon group of 4 to 20 carbon atoms.

Alternatively, the sulfonated polyarylene may be

produced by hydrolysis of a polyarylene resulting from

copolymerization of the aromatic sulfonate derivative of the

formula (E) with at least one compound having the aforesaid

20   formula (A).

For example, the electrolyte membrane for use in the

invention may be produced by a film casting method in which

a proton conductive polymer such as the aforesaid sulfonated

polymer is dissolved in an organic solvent and the solution

is flow-cast over a substrate to form a film. The substrate

5   used herein is not particularly limited and may be selected

from those substrates commonly used in the film casting methods.

Examples thereof include plastic substrates and metal

substrates. For example, thermoplastic resin substrates such

as polyethyleneterephthalate (PET) films are preferable.

10   The organic solvents to dissolve the proton conductive

polymer include aprotic polar solvents such as

N-methyl-2-pyrrolidone, N,N-dimethylformamide,

γ-butyrolactone, N,N-dimethylacetamide, dimethylsulfoxide

and dimethylurea. Of these, N-methyl-2-pyrrolidone is

15   preferable in terms of solvent properties and solution

viscosity. These aprotic polar solvents may be used singly

or in combination of two or more kinds.

           The organic solvent for dissolving the proton conductive

polymer may be a mixed solvent of the above aprotic polar

20   solvent and an alcohol. Exemplary alcohols include methanol,

ethanol, propyl alcohol, isopropyl alcohol, sec-butyl alcohol

and tert-butyl alcohol. In particular, methanol is preferable

since it ensures an appropriately low solution viscosity over

a wide range of proportions of the proton conductive polymer.

These alcohols may be used singly or in combination of two or more kinds.

The above mixed solvent will contain the aprotic polar solvent in an amount of 95 to 25 wt%, and preferably 75 to 25

5   wt%, and the alcohol in an amount of 5 to 75 wt%, and preferably 25 to 75 wt% (the total of these two is 100 wt%). This proportion of the alcohol leads to an appropriately low solution viscosity.

Although the concentration of the proton conductive

10 polymer in the solution (i.e. the polymer concentration) depends on the molecular weight of the polymer, it is generally between 5 and 40 wt%, and preferably between 7 and 25 wt%. The polymer concentration less than 5 wt% causes difficulties in producing the membrane in large thickness and results in easy

15 occurrence of pinholes. On the other hand, when the polymer concentration exceeds 40 wt%, the solution viscosity becomes so high that the production of membrane from the solution will be difficult and further that the obtained film may have low surface smoothness.

20   The solution viscosity may vary depending on the molecular weight of the proton conductive polymer or the polymer concentration. Generally, it is between 2,000 and 100,000 mPa·s, and preferably between 3,000 and 50,000 mPa·s. When the viscosity is less than 2,000 mPa·s, the solution will

have too high a fluidity and may spill out of the substrate

during the membrane production. On the contrary, the

viscosity over 100,000 mPa·s is so high that the solution cannot

be extruded through a die and the flow-casting for the film

5   production may be difficult.

Preferably, the wet film obtained as above will be soaked

in water to substitute the remaining organic solvent in the

film with water. The amount of the residual solvent in the

proton conductive membrane can be reduced by this treatment.

10   Prior to the soak in water, the wet film may be predried.

The predrying may be carried out by leaving the wet film at

50 to 150°C for 0.1 to 10 hours.

Soaking the wet films in water may be carried out

batchwise with respect to each sheet, or may be a continuous

15   process where the films in the original form of laminate with

a substrate film (e.g. PET film) as produced are soaked in water

and wound sequentially.

In the batchwise soaking, the films are suitably framed

or fixed by similar means to prevent wrinkles from forming on

20   the surface of treated films.

The soaking should be suitably made so that the wet films

would contact with water that is at least 10 parts by weight,

and preferably at least 30 parts by weight based on 1 part by

weight of the wet films. This contact ratio is suitably set

as large as possible to minimize the amount of solvent remaining in the electrolyte membrane. For the purpose of reducing the residual solvent amount, it is also effective to keep the concentration of the organic solvent in water at or below a

5 certain level by renewing the water used in the soaking or by letting the water overflow. The in-plane distribution of the organic solvent within the electrolyte membrane may be effectively uniformed by homogenizing the organic solvent concentration in the water by stirring or the like.

10   When the wet film is soaked in water, the water preferably has a temperature of 5 to 80°C. Although the substitution between the organic solvent and water can take place at a higher rate as the water temperature rises, the water absorption in the film will also increase at higher temperatures.

15 Accordingly, there is a concern that the electrolyte membrane has a rough surface after dried. In general, the water temperature is suitably between 10 and 60°C from the viewpoints of the substitution rate and handling properties.

       The soaking time varies depending on the initial amount

20 of residual solvent, the water-solvent contact ratio and the water temperature. Generally, the soaking time ranges from 10 minutes to 240 hours, and preferably from 30 minutes to 100 hours.

Drying the water-soaked wet film gives an electrolyte membrane having a reduced amount of residual organic solvent, which is generally 5 parts by weight or less based on 100 parts by weight of the proton conductive polymer.

5   Controlling the soaking conditions enables reduction of the residual solvent to 1 part by weight or less based on 100 parts by weight of the proton conductive membrane. For example, this is possible when the wet film is soaked in water that is at least 50 parts by weight based on 1 part by weight of the wet film, at a water temperature of 10 to 60°C over a period of 10 minutes to 10 hours.

When the electrolyte membrane contains a large amount of the residual organic solvent such as the polar solvent, it will have poorer heat resistance due to the function of the polar solvent as plasticizer, and will also cause cells to take a very long time until stable electricity generation. Furthermore, the solvent can be removed by thermal changes during electricity generation to produce contraction stress, which causes a permanent set in the film. Such strained films can be cracked by some shocks and the cell may be deformed. With these expected problems in consideration, the residual organic solvent is preferably reduced to 5 parts by weight or less.

After the wet film has been soaked in water as described

above, the film will be dried at 30 to 100°C, preferably 50

to 80°C, for 10 to 180 minutes, preferably 15 to 60 minutes.

Subsequently, it will be dried at 50 to 150°C and under

atmospheric pressure or in vacuo, preferably at 500 to 0.1 mmHg,

5   for 0.5 to 24 hours. The electrolyte membrane according to

the invention may be thus obtained.

The electrolyte membrane obtained as described above

will range in dry thickness from 10 to 100µm, and preferably

from 20 to 80µm.

10   (Good solvent for electrolyte membrane)

The good solvent for the electrolyte membrane will be

preferably an aprotic dipolar solvent having a dielectric

constant of 20 or more, and preferably 30 or more.

When the aprotic dipolar solvent has a dielectric

15   constant of 20 or more, the electrolyte membrane and the

electrode substrates may be combined with sufficient adhesion

to form a satisfactory membrane-electrode assembly.

On the other hand, when the dielectric constant is below

20, the adhesion among the electrolyte membrane and the

20   electrode substrates becomes insufficient to cause problems

such as lower generating performance.

The suitable aprotic dipolar solvents include

N,N-dimethylformamide (boiling point: 153°C, dielectric

constant: 36.71), N,N-dimethylacetamide (166°C, 37.78),

N-methyl-2-pyrrolidone (202°C, 32), γ-butyrolactone (204°C, 39), tetramethylurea (177°C, 30 or more), dimethylsulfoxide (189°C, 46.68), hexamethylphosphoric triamide (233°C, 30) and sulfolane (287°C, 43.3).

5   These dielectric constants are based on the data described in Organic Solvents (written by Riddick and Bunger, published from Wiley-Interscience, 1970).

(Manufacturing process)

In the invention, the good solvent for the electrolyte

10   membrane is applied to at least one, and preferably both of the facing surfaces of the opposed electrolyte membrane and the electrode substrate. The application method is not particularly limited if it can spread the solvent uniformly over the facing surface(s) of the opposed electrode substrate

15   and the electrolyte membrane. Exemplary methods include spray coating with air guns, airless guns and aerosol sprays, dip coating, flow coating, brush coating and sponge coating.

The good solvent will be usually applied in an amount of 0.001 to 10 mg/cm^2, and preferably 0.01 to 1 mg/cm^2. When

20   this amount is too small, the adhesion between the electrolyte membrane and the electrode substrate may be unfavorably bad. On the other hand, too high an amount leads to swelling and dissolution of the electrolyte membrane, resulting in deformation.

Subsequently, the electrode substrates and the electrolyte membrane are pressure bonded. The pressure bonding for the electrode substrates and the electrolyte membrane may be performed using an apparatus capable of

5   pressing and heating. For example, a hot press or a roller press may be suitably employed. The pressure bonding should be carried out at temperatures higher than the glass transition temperature of the electrolyte membrane, and is generally between 80 and 200°C. The pressure in the pressure bonding

10   depends on the thickness of the electrode membranes and the like, but is generally in the range of 0.5 to 20 MPa.

EXAMPLES

The present invention will be hereinafter described in

15   more detail by the following Examples, but it should be construed that the invention is in no way limited to those Examples.

The residual amount of N-methyl-2-pyrrolidone (NMP) was determined as described below.

20   [Residual NMP amount]

The proton conductive membrane was dissolved in DMSO-d6, and the solution was subjected 128 times to integrating measurement of ^{1}H-NMR. The amount (parts by weight) of NMP per 100 parts by weight of the polymer was determined from a

ratio of the peak intensity of NMP to that of the polymer.

[Production Example]

[Synthesis of sulfonated polyarylene]

(Preparation of oligomer)

5   A 1-liter, three-necked flask equipped with a stirrer,

a thermometer, a condenser tube, a Dean-Stark tube and a

three-way nitrogen inlet cock was charged with:

        67.3g (0.20 mol) of 2,2-bis(4-hydroxyphenyl)-

1,1,1,3,3,3-hexafluoropropane (bisphenol AF),

10   60.3g (0.24 mol) of 4,4'-dichlorobenzophenone

(4,4'-DCBP),

        71.9g (0.52 mol) of potassium carbonate,

        300 ml of N,N-dimethylacetamide (DMAc), and

        150 ml of toluene.

15   The flask was placed in an oil bath, and the contents

were heated at 130°C with stirring in a nitrogen atmosphere.

Water yielded during the reaction was allowed to form an

azeotropic mixture with toluene and removed outside the system

through the Dean-Stark tube. The generation of water almost

20 ceased in about 3 hours. Then the reaction temperature was

raised gradually from 130°C to 150°C, during which most of the

toluene was removed. After the reaction was continued at 150°C

for 10 hours, 10.0g (0.040 mol) of 4,4'-DCBP was added and the

reaction was continued for another 5 hours. The reaction

solution thus obtained was allowed to cool naturally and

filtered to remove the precipitate consisting of by-product

inorganic compounds. The filtrate was poured into 4 liters

of methanol. The precipitated reaction product was filtered

5   off, dried and dissolved in 300 ml of tetrahydrofuran. The

thus-formed solution was poured into 4 liters of methanol to

precipitate an objective compound. The compound weighed 95g

(85% yield).

The above-obtained polymer had a number-average

10   molecular weight in terms of polystyrene of 9,900 as measured

by GPC (THF solvent). The polymer was found to be soluble in

THF, NMP, DMAc, sulfolane and the like. The glass transition

temperature (Tg) and heat decomposition temperature thereof

were 110°C and 498°C respectively.

15   The polymer obtained above was expected to have a

structure represented by the following formula (I):
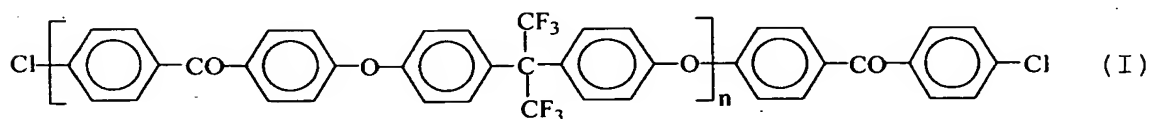
20   (Synthesis of copolymer containing polyarylene)

A flask was charged with:

· 28.4 g (2.87 mmol) of the oligomer having the formula

(I),

29.2 g (67.1 mmol) of

2,5-dichloro-4'-(4-phenoxy)phenoxybenzophenone (DCPPB),

1.37 g (2.1 mmol) of bis(triphenylphosphine)nickel

dichloride,

5   1.36 g (9.07 mmol) of sodium iodide,

7.34 g (28.0 mmol) of triphenylphosphine, and

11.0 g (168 mmol) of zinc powder.

Inside the flask had been purged with dried nitrogen,

130 ml of N-methyl-2-pyrrolidone was added and the mixture was

10   heated to 80°C, followed by stirring for 4 hours to carry out

polymerization. The resultant polymerization solution was

diluted with THF and was poured into hydrochloric

acid/methanol to precipitate a copolymer. Subsequently, the

copolymer was recovered, repeatedly washed with methanol,

15   dissolved in THF, and reprecipitated in methanol. Thus

purified copolymer was filtered off and vacuum dried to give

an objective copolymer in an amount of 50.7 g (96% yield). GPC

(THF solvent) provided that the copolymer had a number-average

molecular weight of 40,000 and a weight-average molecular

20   weight of 145,000, both in terms of polystyrene.

(Preparation of sulfonated polymer)

A 25-g portion of the copolymer obtained above was placed

in a 500 ml separable flask and 250 ml of a 96% sulfuric acid

solution was added thereto, followed by stirring for 24 hours

in a stream of nitrogen. The resultant solution was poured

into a large amount of ion-exchange water to precipitate a

polymer. The polymer was repeatedly washed with water until

the pH in the used water reached 5, and was thereafter dried

5   to give a sulfonated polymer in an amount of 29 g (96%). GPC

(NMP solvent) provided that the sulfonated polymer had a

number-average molecular weight of 67,000 and a weight-average

molecular weight of 277,000, both in terms of polystyrene.

[Example 1]

10   The sulfonated polyarylene copolymer was dissolved in

a mixed solvent consisting of NMP and methanol (1/1 weight

ratio) with 15 wt% copolymer concentration. The solution was

flow cast on a PET film and dried for 1 hour in a 120°C oven

with internal air circulation to give a membrane having a

15   thickness of 40μm. Twenty A4 specimens cut from the membrane

were soaked in 100 liters of distilled water over a period of

48 hours, and were dried for 1 hour in a 80°C oven with internal

air circulation. Thus, proton conductive membranes having a

residual NMP amount of 0.5 part by weight were obtained.

20   Each proton conductive membrane was sandwiched between

catalyzed electrode substrates, in which NMP had been sprayed

on catalyst/carbon surfaces (EC-20-20-10 available from TOYO

TECHNICA INC., catalyst amount = 1 mg/cm^2, 20 wt% platinum

supported on Vulcan XC-72), so that both the catalyst/carbon

surfaces would contact with the proton conductive membrane.

They were hot pressed at 160°C and 2.45 MPa for 15 minutes to

form a membrane-electrode assembly (MEA) consisting of the

proton conductive membrane and the catalyzed electrode

5   substrates.

This MEA was placed in a thermo-hygrostat under the

conditions of 85°C and 90% RH similar to those in practical

working conditions for fuel cells.   No defects were caused in

the interfaces between the proton conductive membrane and the

10   catalyzed electrode substrate in the following 5000 hours.

[Example 2]

MEA was manufactured by the procedure illustrated in

Example 1 except that the catalyst/carbon surfaces were coated

with N,N-dimethylacetamide (DMAC) in place of NMP.   This MEA

15   was placed in a thermo-hygrostat under the conditions of 85°C

and 90% RH similar to those in practical working conditions

for fuel cells.   No defects were caused in the interfaces

between the proton conductive membrane and the catalyzed

electrode substrate in the following 5000 hours.

20   [Example 3]

MEA was manufactured by the procedure illustrated in

Example 1 except that the catalyst/carbon surfaces were coated

with dimethylsulfoxide in place of NMP.   This MEA was placed

in a thermo-hygrostat under the conditions of 85°C and 90% RH

similar to those in practical working conditions for fuel cells.

No defects were caused in the interfaces between the proton

conductive membrane and the catalyzed electrode substrate in

the following 5000 hours.

5   [Comparative Example 1]

MEA was manufactured by the procedure illustrated in

Example 1 except that no solvent was applied to the

catalyst/carbon surfaces. This MEA was placed in a

thermo-hygrostat under the conditions of 85°C and 90% RH

10   similar to those in practical working conditions for fuel cells.

Separation was caused in the interfaces between the proton

conductive membrane and the catalyzed electrode substrate in

10 hours.

[Comparative Example 2]

15   MEA was manufactured by the procedure illustrated in

Example 1 except that tetrahydrofuran (dielectric constant:

7.58) was applied to the catalyst/carbon surfaces. This MEA

was placed in a thermo-hygrostat under the conditions of 85°C

and 90% RH similar to those in practical working conditions

20   for fuel cells. Separation was caused in the interfaces

between the proton conductive membrane and the catalyzed

electrode substrate in 15 hours.

EFFECT OF THE INVENTION

The invention enables production of membrane-electrode assemblies with sufficient bond strength among an electrolyte membrane and electrode substrates even if the electrolyte membrane is made from a heat resistant material such as an aromatic polymer.